Japanese Examined Patent Publication

7-118592

Title: WATER-BASE INK WITH METALLIC LUSTER FOR BALL-POINT PENS

Abstract

Constitution: The ink has a viscosity (measured with a type E viscometer at an ST rotor speed of 1rpm, at 25 deg.C) of 10,000 to 150,000 cps and contains at least a pearlescent pigment in an amount of 5 to 20wt.%, water-soluble thickening resins comprising, e.g. a seed polysaccharide,including guar gum or locust bean gum, the derivative thereof, or a microbial xanthan gum, a water-soluble organic solvent, including glycol or glycerin, preferably in an amount of 5 to 40wt.% and water.

Object: To obtain the title ink which gives a well-defined handwriting with metallic luster and has good long-term stability without deterioration even in long-term storage.

What is claimed

Claim 1: A water-base ink with metallic luster for ball-point pens comprising at least a pearlescent pigment, a water-soluble thickening resin, a solvent, and water, wherein the ink has a viscosity (measured with a type E viscometer at an ST rotor speed of 1rpm, at 25 deg.C) of 10,000 to 150,000 cps.

EXHIBIT A

Detailed description of the invention

Field of industrial application

The present invention relates to a water-base ink for ball-point pens with metallic luster capable of obtaining an ink which gives a well-defined handwriting with metallic luster including gold and silver by using a pearlescent pigment. The present invention also relates to a water-base ink for ball-point pens with metallic luster capable of obtaining a handwriting with long-term stability without deterioration even in long-term storage having good discharge property of the ink.

Prior art

Heretofore, for the purpose of obtaining a handwriting with metallic luster such as gold and silver, varieties of inks using aluminum powder pigments, bronze powder pigments, and pearlescent pigments have been proposed. For example, Japanese Examined Patent Publication No. 62-037678 discloses a double-color ink composition comprising a metal powder pigment including an aluminum powder, an oil-soluble dye, a resin, and a solvent and generating the outline effect with dyes permeating and dispersing around the hand writings formed by metallic powder pigments. Japanese Examined Patent Publication No. 1-056109 discloses an ink with metallic luster for marking pens comprising a

metal fine powder including an aluminum powder with surface treatment and having smooth fluidity of the ink from various marking pens, and having easy dispersibility in practical use. In addition, Japanese Unexamined Patent Publication No. 60-186573 discloses an oily ink with metallic luster without containing water, characterized as comprising a solvent, a thickening resin soluble to the said solvent, a metal powder pigment and coloring pigment at least in a required amount and having a high viscosity of at least a required value. This ink is suitable in use for pressurizing ball-point pens.

Further, Japanese Unexamined Patent Publication No. 1-210478 discloses a water-base metallic ink comprising the main components of the ink including a resin, an aluminum paste, and water, to which acetylene alcohol derivatives are added as additives with the aim of preventing the dirt of coating by pin holes. Japanese Unexamined Patent Publication No. 5-117569 discloses a water-base ink using a pearlescent pigment which is stable to water, instead of using metal powder pigment.

Problem to be solved by the invention

The water-base inks with metallic luster which can be used for ball-point pens have not been proposed so far. As for inks for

ball-point pens, it is necessary to use the said inks without redispersing the pigment. Nevertheless, there have been no water-base inks in which no pigments settle. For example, the inks described in Japanese Examined Patent Publications 62-37678 and 1-56109 are oily inks and they are conscious of being used for marking pens. These marking pens are used by containing stirring material including metallic balls in the ink containment chamber, by stirring the writing tools when in use, and by redispersing the settled aluminum powder. In other words, in the ink compositions in these inventions, aluminum powder settles in a short time. In the ink disclosed in Japanese Examined Patent Publication 60-186573, although the amount of the pigment which settles is little, it is an oily ink. In addition, the inventions described in Japanese Examined Patent Publications 1-210478 and 5-117569 are conscious of being used for marking pens as mentioned above although they are water-base inks.

The object of the present invention is to provide a water-base ink with metallic luster for ball-point pens which can preferably be used for long term storage.

The present invention relates to a water-base ink with metallic luster comprising at least a pearlescent pigment, a thickening resin, a solvent, and water, wherein the viscosity of the ink is 10000 to

150000 cps (measured with a type E viscometer at an ST rotor speed of 1rpm, at 25 deg.C).

The detailed explanation goes as follows. A pearlescent pigment used in the present invention is used as a colorant for realizing metallic luster. The pearlescent pigment can be obtained by coating on the surface of natural mica with metallic oxide having high refractive index. The pearlescent pigment with an average particle diameter of 5 to 60μm can preferably be used. When the average particle diameter is less than 5μm, the pearlescent luster lowers and the metallic luster of a handwriting is likely to lower. On the other hand, when the average particle diameter exceeds 60μm, the discharge property is likely to deteriorate when applied to the ball-point pen tip which has been commonly used.

The examples of commercially available pearlescent pigments include Iriodin 100 (average particle diameter: 10 to 60μm, silver), Iriodin 103 (average particle diameter: 10 to 50μm, silver), Iriodin 300 (average particle diameter: 10 to 60μm, gold), Iriodin 302 (average particle diameter: 5 to 20μm, gold), Iriodin 323 (average particle diameter: 5 to 20μm, gold), Iriodin 504(average particle diameter: 10 to 60μm, red), Iriodin 524 (average particle diameter: 5 to 20 μm, red), Iriodin 502 (average particle diameter: 10 to 60μm, copper), Iriodin 520 (average particle diameter: 5 to 20 μm, copper), (manufactured by Merck Japan Limited.) and the like. These pearlescent pigments have acid resistant and alkali resistant

properties, and they are easily dispersed in the water base system although they are insoluble to water. 5 to 20 wt.% of the pearlescent pigment can preferably be used with respect to the water base ink with metallic luster for ball-point pens.

A thickening resin is used in order to prevent pearlescent pigments from settling and to maintain the quality as a water base ink composition for ball-point pens, including prevention of ink leakage out of the pen tip, appropriate discharge of the ink, prevention of dirt at the pen tip and prevention of blotting. As for the ink for ball-point pens that are used in the general atmosphere in which an end of the ink containment tube is open, guar gum, locust bean gum, and derivatives thereof which are seed polysaccharides and xanthan gum which is a microbial polysaccharide are preferably used. In addition, as for pressurizing ball-point pens which are appropriately used for high-speed writing or writing with a pen tip directed upward, the loadings of the said resin can be increased or carageenan, alginic acid and derivatives thereof which are seed polysaccharides and taraganth gum, cellulosic derivatives, synthetic high polymeric polyethylene oxide and polyacrylic acid soda, and the like, can be used. Since the amount of thickening resin to be used differs greatly depending on the kinds of resins, the appropriate viscosity is to be set. The said viscosity is 10000 to 150000cps (measured with a type E viscometer at an ST rotor speed of 1rpm, at 25 deg.C). In addition, when the inks are used for ball-point pens, since the lowering of the

ink viscosity by the shear force of the ball rotation affects the amount of the ink discharge of the pen-tip, it is preferable that the ratio of the viscosity at a speed of 1rpm to the measured value at a speed of 10rpm is not less than 3.0.

A water-soluble organic solvent is used in order to maintain the various qualities of a water-base ink for ball-point pens, including prevention of drying of the ink at the pen-tip and prevention of freezing of the ink at a low temperature. To be specific, glycols including ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, polyethylene glycol, 1,3 butylene glycol, thiodiethylene glycol, glycerin, and the like, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, 2-pyrrolidone, triethanol amine, and the like can be used alone or in combinations. The preferable amount to be used is 5 to 40 wt.% with respect to the total amount of the water-base ink with metallic luster.

Water is used as a main solvent.

In addition to the above mentioned components, wetting agents including urea, ethylene urea, thio urea, and the like, lubricants, antiseptic mildew proofing agents including benzotriazoline types, omazine types and the like, rust inhibitors including benzotriazole, and the like, additives including anionic or nonionic surfactants, and the like. Further, in order to realize hues of vaious kinds of metallic luster colors, dyes including acid dyes, basic dyes, and direct dyes, and the like, and colored pigments can be used.

In producing the water-base ink with metallic luster of the present invention, various kinds of heretofore known methods can be used. For example, the ink can easily be obtained by compounding the said components, followed by stirring and mixing with a mixer including a Henschel mixer, and mixing and introducing attrition by a dispersing machine including a ball mill, or the like.

Working effect

As to whether the water-base ink with metallic luster for ball-point pens of the present invention has an effect in preventing the pearlescent pigments from settling and in showing the stability over a long period of time in long-term storage, it can be inferred as follows. Since the viscosity of the ink composition for ordinary ball-point pens of the present invention is high enough not to damage the fluidity of the ink, pearlescent pigments are fixed between resins, thereby preventing the settling of the pearlescent pigments. In addition, since pearlescent pigments do not cause gelation, hydrolysis, and partial insolubilization, the viscosity of the ink does not increase or decrease.

Example

Example 1

Iriodin 302 (manufactured by Merck Japan Limited) 10.0 parts by weight

Jaguar CMHP (guar gum derivative, manufactured by Sansho Co., Ltd.)

1.0 parts by weight

Ethylene glycol 15.0 parts by weight

Glycerin 10.0 parts by weight

Water 62.9 parts by weight

Proxel XL-2 (anti-mildew proofing agent, manufactured by ICI Japan, Co., Ltd.)

0.1 parts by weight

NP-10 (dispersant, manufactured by Nikko Chemicals, Co., Ltd.)

1.0 parts by weight

All the components described above except for Jaguar CMHP were put into a ball mill and after the dispersing treatment for 10 hours, Jaguar CMHP was added and treated for another hour, thereby obtaining a gold color ink with the viscosity of 25000 cps (E viscometer at a speed of 1rpm, at 25 deg.C). When this gold color ink was packed in a transparent ink container tube comprising a hollow casing made of polypropylene to which a ball-point pen (nickel silver ball-point pen tip (material of the ball: carbide alloy)is directed at one end and was written on a sheet of paper, a well-defined gold color hand writing free of blur was obtained. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 3.6.

Example 2

Iriodin 103 (manufactured by Merck Japan Limited) 10.0 parts by weight

Locust bean gum 2.0 parts by weight

Propylene glycol 20.0 parts by weight

Ethylene glycol 10.0 parts by weight

Water 56.9 parts by weight

Proxel GXL-2 (anti-mildew proofing agent, manufactured by ICI Japan, Co., Ltd.) 0.1 parts by weight

BT-12 (dispersant, manufactured by Nikko Chemicals, Co., Ltd.) 1.0 parts by weight

All the components described above were put into a ball mill followed by the dispersing treatment for 12 hours, thereby obtaining a silver color ink with the viscosity of 35000 cps (E viscometer at a speed of 1rpm, at 25 deg.C). When this silver color ink was packed in a ball-point pen as in Example 1 and was written on a sheet of paper, a well-defined silver color hand writing free of blur was obtained. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 3.1.

Example 3

Iriodin 524 (manufactured by Merck Japan Limited) 10.0 parts by weight

Xanthan gum 1.0 parts by weight

Ethylene glycol 10.0 parts by weight

Glycerin 10.0 parts by weight

Water 67.9 parts by weight

Proxel XL-2 (anti-mildew proofing agent, manufactured by ICI Japan, Co., Ltd.) 0.1 parts by weight

NP-10	1.0 parts by weight

All the components described above were put into a ball mill followed by the dispersing treatment for 2 hours, thereby obtaining a red color ink with metallic luster with the viscosity of 30000 cps (E viscometer at a speed of 1rpm, at 25 deg.C). When this red ink was packed in a ball-point pen as in Example 1 and was written on a sheet of paper, a well-defined red color hand writing with metallic luster free of blur was obtained. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 6.0.

Example 4

Iriodin 302	10.0 parts by weight
Hydoxyethylcellulose	5.0 parts by weight
Ethylene glycol	17.0 parts by weight
Glycerin	8.0 parts by weight
Water	61.9 parts by weight
Proxel GXL	0.1 parts by weight
NP-10	1.0 parts by weight

All the components described above were put into a ball mill followed by the dispersing treatment for 3 hours, thereby obtaining a gold color ink with the viscosity of 110000 cps (E viscometer at a speed of 1rpm, at 25 deg.C). When this gold ink was packed in an ink containment tube comprising a casing made of stainless steel to which a pressurizing ball-point pen (stainless steel ball-point pen tip (material of the ball: carbide alloy))is directed at one end,

thereafter sealed at the tail plug by applying pressure of 3.0/cm² in the said ink containment tube and was written on a sheet of paper, a well-defined gold color hand writing free of blur was obtained.

Comparative Example 1

A gold ink with the viscosity of 7000 cps (E viscometer at a speed of 1rpm, at 25 deg.C)was obtained by the same method of Example 1 except that the amount of Jaguar CMHP was reduced to 0.6 parts by weight and added by the same amount of water. When this gold color ink was packed in the ball-point pen as in Example 1 and was written on a sheet of paper, a well defined gold handwriting free of blur was obtained. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 2.5.

Comparative Example 2

A gold ink with the viscosity of 180000 cps (E viscometer at a speed of 1rpm, at 25 deg.C) was obtained by the same method of Example 1 except that the amount of Jaguar CMHP was increased to 2.8 parts by weight and reduced by the same amount of water. When this gold color ink was packed in the ball-point pen as in Example 1 and was written on a sheet of paper, writing was impossible. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 5.0.

Comparative Example 3

A silver ink with the viscosity of 36000 cps (E viscometer at a speed of 1rpm, at 25 deg.C) was obtained by the same method of Example 2 except that aluminum powder (WB0230, manufactured by Toyo Aluminium Co., Ltd.) was used instead of Iriodine 103 in Example 2. When this

silver color ink was packed in the ball-point pen as in Example 1 and was written on a sheet of paper, a well-defined silver colored hand writing free of blur was obtained. Here, the viscosity ratio of this ink at a speed of 1 to 10 rpm was 3.2.

As for water-base inks with metallic luster for ball-point pens, the tests on viscosity change, on writing performance, and on settling were conducted. The results were shown in the Table 1.

Table 1.

	Viscosity change		Writing performance		Settling
	Right after	With time	Right after	With time	
Example 1	250	200	○	○	0/90
Example 2	350	310	○	○	0/90
Example 3	300	260	○	○	0/90
Example 4	1100	1000	○	○	0/90
Comparative Example 1	70	---	×	---	---
Comparative Example 2	1800	1500	△	△	0/90
Comparative Example 3	360	98	○	×	70/90

(Notes on Table 1)

Comparative Example 1: Test on viscosity change could not be measured due to the settlement of pearlescent pigments;

Test on writing could not be measured due to the settling of the pearlescent pigments at the time of centrifuging and degassing;

Test on settlement could not be measured due to the settlement of the pearlescent pigments at the time of centrifuging and degassing .

Test on viscosity change: Viscosity was measured right after the adjustment of the ink and later (with time).

Measurement condition:Measured with a type E viscometer at an ST rotor speed of 1rpm, at 25 deg.C / unit(poise)

Leaving condition (with time): The ink was put into the screw-mouthed bottle and was left for 1 month in the isothermal room at 50 deg.C.

Test on writing performance: A handwriting right after the writing sample was produced and a handwriting later (with time) were observed.

Writing sample: 0.8 g of the ink was directly packed into a transparent ink containment tube comprising a hollow casing made of polypropylene to which a ball-point pen tip is directed at one end, followed by filling 0.1 g of back-flow preventive agent on the upper part, thereafter centrifuging and degassing. It is noted, however, as for the ink obtained in Example 4, 0.8 g of the ink was packed into an ink containment tube comprising a casing made of stainless steel to which a stainless steel ball-point pen tip (material of the ball: carbide alloy) is directed at one end, followed by applying pressure of 3.0 kg/cm^2 in the ink containment tube.

Writing paper: High quality paper(JIS 3201 writing paper A) was used.

Leaving condition (with time): The ink was left with the pen tip directed downward in the isothermal room at 50 deg.C for 1 month.

Evaluation

Rating criteria are:

○ for capable of writing preferably.

△ for showing thin spots.

× for incapable of writing.

Test on the degree of settling: Supernatant liquid of the ink after it was left (later, with time) was measured.

Sample

Leaving condition (with time): The ink was left in the isothermal room at 50 deg.C.

Evaluation

Length of supernatant liquid/ length of the ink tube

Effect of the invention

As explained in detail so far, the water base ink with metallic luster for ball-point pens of the present invention provides well-defined metallic luster to the hand writing, has a good long-term stability without deterioration even in long-term storage, which is capable of achieving the object of the present invention fully and therefore useful.

FIG. 1

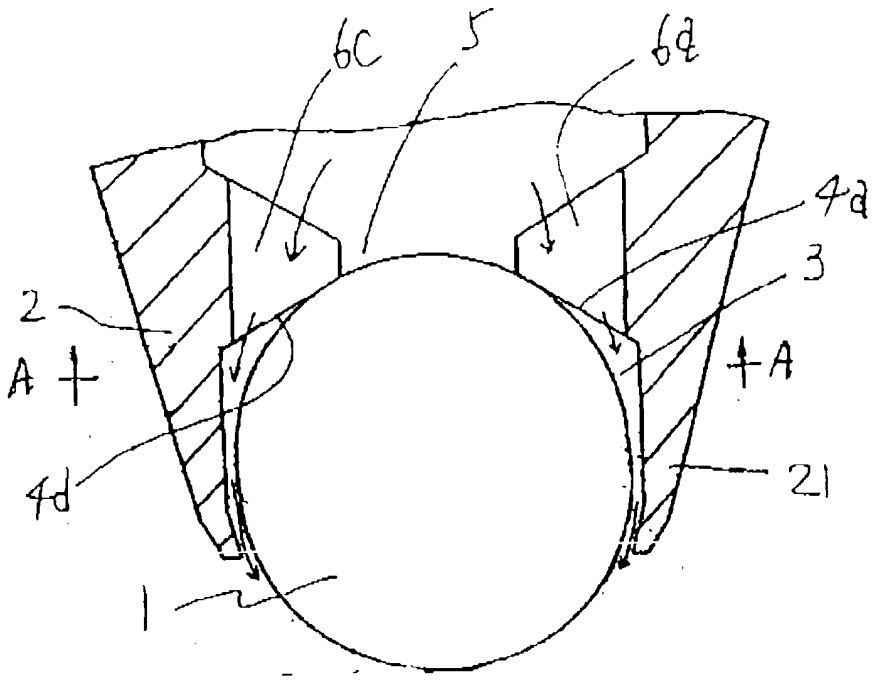

FIG. 2

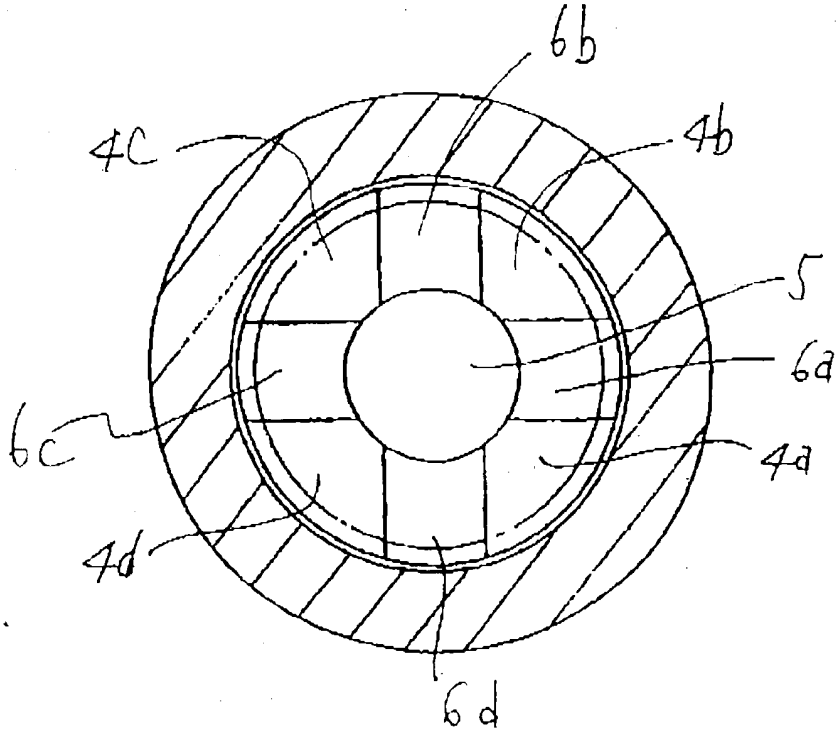

EXHIBIT B